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In re Patent Application of:

Shunpei YAMAZAKI et al.

Serial No. 10/733,352

Filed: December 12, 2003

For: PROCESS FOR PRODUCING A
PHOTOELECTRIC CONVERSION
DEVICE

) Group Art Unit: 2812

) Examiner: S. Isaac

CERTIFICATE OF MAILING

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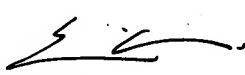
Honorable Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Further to the Response filed on August 22, 2005, Applicant submits herewith a verified English translation of priority Japanese Application No. 2001-022471 filed January 30, 2001.

Applicant respectfully submits that the 103 rejection has been overcome with the submission of the verified English translation. Reconsideration and withdrawal of the rejection under 103 is requested.

Respectfully submitted,


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CONVERSION DEVICE)

VERIFICATION OF TRANSLATION

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Sir:

I, Mika Tatsumi, C/O Semiconductor Energy Laboratory Co., Ltd. 398, Hase, Atsugi-shi, Kanagawa-ken 243-0036 Japan, herewith declare:

that I am well acquainted with both the Japanese and English Languages;

that I am the translator of the attached translation of the Japanese Patent Application No. 2001-022471 filed on January 30, 2001; and

that to the best of my knowledge and belief the following is a true and correct translation of the Japanese Patent Application No. 2001-022471 filed on January 30, 2001.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: this 3rd day of October 2005

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Name: Mika Tatsumi

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Filing Date: January 30, 2001
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[List of Attachment]

[Attachment]	Specification	1
[Attachment]	Drawing	1
[Attachment]	Abstract	1

5 [Proof] required

[Document Name] Specification

[Title of the Invention] METHOD FOR PRODUCING A PHOTOELECTRIC
CONVERSION DEVICE

5 [Scope of Claim]

[Claim 1]

A method for producing a photoelectric conversion device, characterized by
comprising:

10 a first step of forming a first semiconductor film having an amorphous
structure;

a second step of adding a catalyst element for promoting crystallization to the
semiconductor film having the amorphous structure and conducting a first heat
treatment to form a first semiconductor film having a crystal structure;

15 a third step of forming a second semiconductor film containing a rare gas
element over the first semiconductor film having the crystal structure;

a fourth step of conducting a second heat treatment to move the catalyst
element into the second semiconductor film; and

a fifth step of removing the second semiconductor film.

[Claim 2]

20 A method for producing a photoelectric conversion device, characterized by
comprising:

a first step of forming a first semiconductor film having an amorphous
structure;

a second step of adding a catalyst element for promoting crystallization to the

semiconductor film having the amorphous structure and conducting a first heat treatment to form a first semiconductor film having a crystal structure;

a third step of forming a barrier layer over a surface of the first semiconductor film having the amorphous structure;

5 a fourth step of forming a second semiconductor film containing a rare gas element over the barrier layer,

a fifth step of conducting a second heat treatment to move the catalyst element into the second semiconductor film, and

a sixth step of removing the second semiconductor film.

10 [Claim 3]

A method for producing a photoelectric conversion device, characterized by comprising:

a first step of forming a first semiconductor film having an amorphous structure;

15 a second step of adding a catalyst element for promoting crystallization to the semiconductor film having the amorphous structure and conducting a first heat treatment to form a first semiconductor film having a crystal structure;

a third step of forming a second semiconductor film over the first semiconductor film having the crystal structure;

20 a fourth step of adding a rare gas element to the second semiconductor film;

a fifth step of conducting a second heat treatment to move the catalyst element into the second semiconductor film, and

a sixth step of removing the second semiconductor film.

[Claim 4]

A method for producing a photoelectric conversion device, characterized by comprising:

a first step of forming a first semiconductor film having an amorphous structure;

5 a second step of adding a catalyst element for promoting crystallization to the semiconductor film having the amorphous structure and conducting a first heat treatment to form a first semiconductor having a crystal structure;

a third step of forming a barrier layer over a surface of the first semiconductor film having the amorphous structure;

10 a fourth step of forming a second semiconductor film over the barrier layer;

a fifth step of adding a rare gas element to the second semiconductor film;

a sixth step of conducting a second heat treatment to move the catalyst element into the second semiconductor film; and

a seventh step of removing the second semiconductor film.

15 [Claim 5]

A method for producing a photoelectric conversion device according to claim 1 or 2, characterized in that the second semiconductor film is formed by a sputtering method.

[Claim 6]

20 A method for producing a photoelectric conversion device according to claim 1 or 2, characterized in that the second semiconductor film is formed by a plasma CVD method.

[Claim 7]

A method for producing a photoelectric conversion device according to claim 3

or 4, characterized in that the rare gas element is added by an ion implantation method or an ion doping method.

[Claim 8]

A method for producing a photoelectric conversion device according to claim 2 or 4, characterized in that the barrier layer is forming a chemical oxide film by ozone water.

[Claim 9]

A method for producing a photoelectric conversion device according to claim 2 or 4, characterized in that the barrier layer is formed by oxidizing a surface by plasma treatment.

[Claim 10]

A method for producing a photoelectric conversion device according to claim 2 or 4, characterized in that the barrier layer is formed by oxidizing a surface with ozone generated by irradiation of ultraviolet rays in an atmosphere containing oxygen.

[Claim 11]

A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the first heat treatment is conducted by radiation from one kind or more kinds selected from a halogen lamp, a metal halide lamp, a xenon arc lamp, a carbon arc lamp, a high-pressure sodium lamp, and a high-pressure mercury lamp.

[Claim 12]

A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the first heat treatment is conducted by a furnace annealing method using an electrically heating furnace.

[Claim 13]

A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the second heat treatment is conducted by radiation from one kind or more kinds selected from a halogen lamp, a metal halide lamp, a xenon arc lamp, a carbon arc lamp, a high-pressure sodium lamp, and a high-pressure mercury lamp.

[Claim 14]

A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the second heat treatment is conducted by a furnace annealing method using an electrically heating furnace.

10 [Claim 15]

A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the rare gas is one kind or more kinds selected from He, Ne, Ar, Kr and Xe.

[Claim 16]

15 A method for producing a photoelectric conversion device according to claims 1 to 4, characterized in that the catalyst element is one kind or more kinds selected from Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, Cu and Au.

[Detailed Description of the Invention]

[0001]

20 [Technical Field to which the Invention pertains]

The present invention relates to a photoelectric conversion device wherein a photoelectric conversion layer composed of a crystalline silicon film is formed on a substrate, and a method for producing the same.

[0002]

[Conventional Art]

A photoelectric conversion device can be produced using any one of various semiconductor materials and organic compound materials. However, the photoelectric conversion device is industrially produced using silicon mainly. The photoelectric conversion device using silicon can be classified into a bulk type photoelectric conversion device using a wafer made of monocrystal silicon or polycrystal silicon and a thin film type photoelectric conversion device wherein a silicon film is formed on a substrate. For the bulk type photoelectric conversion device, a semiconductor substrate (such as a silicon wafer) is necessary in the same way as for a LSI (large-scale integrated circuit) or the like. The production amount is limited by the supply capacity thereof. On the other hand, it is considered that potential production capacity of the thin film type photoelectric conversion device is higher because of the use of a semiconductor film on a predetermined substrate.

[0003]

At present, a photoelectric conversion device using amorphous silicon is made practicable. However, it has lower conversion efficiency than the photoelectric conversion device using monocrystal silicon or polycrystal silicon. Furthermore, it has problems such as deterioration by light. Thus, the use thereof is limited to products having a small power consumption, such as a pocket calculator. For development of application aiming sunshine power generation system, photoelectric conversion devices using a silicon film obtained by crystallizing an amorphous silicon film (referred to as a crystalline silicon film hereinafter) have been actively developed.

[0004]

The method of forming the crystalline silicon film is classified into melting recrystallization and solid phase growth methods. In both of the methods, amorphous silicon is formed on a substrate, and this is recrystallized to form a crystalline silicon film. In either case, the substrate is required to endure the crystallization temperature of silicon. Thus, the material which can be used as the substrate is limited. Particularly in the melting recrystallization method, the substrate is limited to a material enduring the melting point of silicon, that is, 1412 °C.

[0005]

The solid phase method is a method of forming an amorphous silicon film on a substrate and then, conducting heat treatment for crystallization. Usually, the amorphous silicon film is hardly crystallized at a temperature of 500 °C or lower. Practically, it is necessary to heat it at 600 °C or higher. For example, in the case that an amorphous silicon film formed by a vapor growth method is heated to be crystallized, a heating time of 10 hours is necessary when heating temperature is 600 °C. On the other hand, when the heating temperature is 550 °C, a heating time of 100 hours or more is necessary.

[0006]

For these reasons, the substrate for forming a crystalline silicon film is required to have high heat-resistance in its own way. It is therefore preferred to use quartz, carbon, a ceramic material or the like for the substrate. However, it is thought that such a substrate is not necessarily suitable for a reduction in production costs. It would be primarily desired that an inexpensive material circulated in a great amount in the market is used for the substrate. However, for example, a #7059 glass substrate

made by Corning Incorporated, which is in general frequently used, has a strain point of 593 °C. Thus, if a conventional crystallizing technique is used, the substrate is distorted to generate large deformation. Therefore, it is not used. Since a substrate of a substance essentially different from silicon is used, a monocrystal film cannot be obtained even if heat treatment for crystallization is merely performed. Thus, only a polycrystal film can be obtained. The grain size of the polycrystal film is difficult to be made large. This fact results in the suppression of an improvement in the efficiency of photoelectric conversion device.

[0007]

As a method for solving the above-mentioned problems, Japanese Patent Laid Open Hei7-58338 discloses a technique wherein a very small amount of a catalyst element is added as a catalyst material for the promotion of crystallization at low temperature to conduct the crystallization. According to the Laid Open Patent gazette, it becomes possible to make heat treatment temperature low and make treatment time short. For example, in the case that the heating temperature is set to 550 °C, it is verified that silicon is crystallized by heat treatment for 4 hours. It is stated that a single element of nickel (Ni), iron (Fe), cobalt (Co) or platinum (Pt), a compound of them and silicon, or the like is suitable for the catalyst element.

[0008]

[Problem to be Solved by the Invention]

Originally, however, all of the catalyst materials used to promote the crystallization are materials unpreferable for crystalline silicon. It is therefore desired that the concentration thereof is as low as possible after the crystallization. The concentration of the catalyst material necessary for promoting the crystallization is a

range from 1×10^{17} to 1×10^{20} /cm³. However, even if the concentration is relatively low, since the element suitable for the catalyst material is a metal, when it is taken in silicon, a defect level is generated. Thus, it is evident that important characteristics for a photoelectric conversion device, such as the lifetime of carriers, deteriorate.

[0009]

Incidentally, it can be considered that the outline of the action principle of a photoelectric conversion device produced by forming a PN junction is as follows. The photoelectric conversion device absorbs light, and generates carriers of electrons and holes by the energy of the absorbed light. About the generated carriers, the electrons move toward its n layer and the holes move toward its p layer by drift and diffusion based on an electric field of junction. In the case that silicon has many defect levels, they are trapped into the defect levels on their way to become extinct. That is, the photoelectric conversion characteristic deteriorates. The time from the generation of the electrons and holes to the extinction thereof is called a lifetime. It is desired that this value is larger for the photoelectric conversion device. Therefore, it is necessary that the amount of impurity elements, which generate the defect level in silicon, are originally as small as possible.

[0010]

An object of the present invention is to provide a photoelectric conversion device wherein the advantage of the crystallization of silicon by the above-mentioned catalyst material is utilized, and further the catalyst material which is unnecessary after the crystallization is removed to exhibit a superior photoelectric conversion characteristic.

[0011]

[Means for Solving the Problem]

In order to solve the above-mentioned problems, a method for producing a photoelectric conversion device of the present invention includes a first step of forming a first semiconductor film having an amorphous structure; a second step of adding a catalyst element for promoting crystallization to the semiconductor film having the amorphous structure and conducting a first heat treatment to form a first semiconductor film having a crystal structure; a third step of forming a second semiconductor film containing a rare gas element over the first semiconductor film having the crystal structure; a fourth step of conducting a second heat treatment to move the catalyst element into the second semiconductor film; and a fifth step of removing the second semiconductor film.

[0012]

By adding, to the first semiconductor film having the amorphous structure, the catalyst element for promoting the crystallization thereof and then conducting the first heat treatment, heating temperature necessary for the crystallization can be made lower than ever before. The catalyst elements that can be used is/are one or more selected from Fe, Ni, Co, Ru, Rh, Pd, Os, Ir, Pt, Cu and Au.

[0013]

The catalyst element remaining in the first semiconductor film after the crystallization can be moved into the second semiconductor film and concentrated and collected by forming the second semiconductor film containing the rare gas element thereon and then conducting the second heat treatment. That is, by incorporating the rare gas element into the second semiconductor film, a strain field can be generated so

as to be a gettering site. Since the rare gas element is not basically bonded to another atom, it is inserted between lattices in the semiconductor film, thereby generating the strain field.

[0014]

5 The gettering technique is well known as a technique for producing an integrated circuit using a silicon monocrystal substrate. As the gettering technique, the following are known: extrinsic gettering, wherein a strain field or a chemical effect is supplied to a silicon substrate from the outside so as to generate gettering effect; and intrinsic gettering, wherein a strain field based on lattice defects with which oxygen
10 generated inside a wafer is concerned is used. The extrinsic gettering includes a method of giving mechanical damage to the back face (the face opposite to the face on which elements are to be formed) of a silicon substrate, and a method of forming a polycrystal silicon film, and a method of diffusing phosphorus. There is also known a
15 gettering technique conducting by forming a strain field is generated by secondary lattice defects formed by ion implantation. The detailed mechanism of the gettering has not been necessarily made clear uniformly. However, the following phenomenon is positively used in the mechanism: when heat treatment is conducted as described above, metal elements are precipitated in the region where a strain field is generated.

[0015]

20 In order to remove the second semiconductor film formed on the first semiconductor film selectively after the gettering is performed, it is advisable to form a barrier layer on the first semiconductor film. The barrier layer may be formed by treating the first semiconductor film with ozone water to form a chemical oxide, by oxidizing the surface thereof by plasma treatment, or by irradiating ultraviolet rays in an

atmosphere containing oxygen to generate ozone and oxidizing the surface therewith.

[0016]

The second semiconductor film is formed by a sputtering method or a plasma CVD method. A rare gas element can be taken in the second semiconductor film by
5 incorporating the rare gas into the sputtering gas or adding the rare gas to the reaction gas. After the formation of the film, it may be added by ion implantation or ion doping. As the rare gas element, one selected from He, Ne, Ar, Kr and Xe is used.

[0017]

The first heat treatment and the second heat treatment are conducted by rapid
10 thermal annealing (Rapid thermal anneal: RTA) using a halogen lamp, a metal halide lamp, a xenon arc lamp, a carbon arc lamp, a high-pressure sodium lamp, or a high-pressure mercury lamp as a heating means or by a furnace annealing method using an electrically heating furnace. In the present invention, it is sufficient that the gettering causes the catalyst element to move at a degree corresponding substantially to
15 the thickness of the semiconductor film. Thus, the gettering can be completely accomplished even by short-time heat treatment such as an RTA method.

[0018]

[Embodiments of the Invention]

[Embodiment 1]

20 Referring to FIG. 1, a method for producing a photoelectric conversion device by forming a catalyst element for promoting the crystallization of silicon adhesively to an amorphous silicon film, crystallizing the amorphous silicon film by heat treatment, and removing the catalyst element remaining after the crystallization outside the crystalline silicon film, is described.

[0019]

In to FIG. 1, a silicon oxide film 102 is formed as a base film on a glass substrate (for example, a 1737 glass substrate made by Corning Incorporated) 101 to have a thickness of 0.3 μm . This silicon oxide film 102 may be formed by a plasma CVD method using tetramethyl silicate (TEOS) as raw material, but a sputtering method
5 CVD method using tetramethyl silicate (TEOS) as raw material, but a sputtering method may be used as another method. Next, an amorphous silicon film (amorphous silicon film) 103 is formed by a plasma CVD method using silane gas as raw material.

[0020]

The formation of the amorphous silicon film 103 may be performed using a
10 reduced-pressure thermal CVD method, a sputtering method or a vacuum evaporation method as well as a plasma CVD method. The amorphous silicon film 103 may be an intrinsic amorphous silicon film to which an element of the 13 or 15 group in the periodic table is not intentionally added, or an amorphous silicon film to which 0.001 to 0.1 atomic% of boron (B) is added. The thickness of the amorphous silicon film 103 is
15 set to 1-20 μm , preferably 5-10 μm (FIG. 1(A)).

[0021]

Next, the substrate is immersed in an aqueous solution wherein hydrogen peroxide water is mixed with ammonia, and is kept at 70 °C for 5 minutes to form an oxidized film (not illustrated) on the surface of the amorphous silicon film 103. This
20 oxidized film is formed to improve the wettability of a solution of nickel acetate in a subsequent step of applying the solution. The nickel acetate solution is applied to the surface of the amorphous silicon film 103 by a spin coating method. In this way, nickel, which will be a catalyst element, is dispersed onto the surface of the amorphous silicon film 103. When the amorphous silicon film 103 is crystallized, nickel acts as a

catalyst for promoting the crystallization.

[0022]

Next, it is kept at a temperature of 450 °C in a nitrogen atmosphere for 1 hour to cause hydrogen in the amorphous silicon film 103 to be released. This is performed to lower the threshold energy for subsequent crystallization by forming dangling bonds intentionally in the amorphous silicon film 103. Thereafter, it is subjected to heat treatment at 500 to 600 °C, preferably at 550 °C, in the nitrogen atmosphere for 4 to 8 hours, so as to crystallize the amorphous silicon film 103. In this way, a crystalline silicon film 104 is formed. Because of the catalyst action of nickel, the temperature for this crystallization can be made to 550 °C. This crystalline silicon film 104 contains 0.001 to 5 atomic % of hydrogen. During the above-mentioned heat treatment, nickel diffuses into silicon so as to form a silicide. In this way, the crystallization of silicon advances.

[0023]

As the method of the heat treatment, there is adopted an RTA method using a halogen lamp, a metal halide lamp, a xenon arc lamp, a carbon arc lamp, a high-pressure sodium lamp, a high-pressure mercury lamp or the like. In the case of performing the RTA method, a heating lamp source is lighted for 1 to 60 seconds, preferably 30 to 60 seconds. This is repeated 1 to 10 times, preferably 2 to 6 times. The emission intensity of the lamp source may be freely decided; however, it is set in such a manner that the semiconductor film is instantaneously heated up to 600 to 1000 °C, preferably 650 to 750 °C. Even if such a high temperature is instantaneously realized, the semiconductor film can be preferentially heated by selecting a lamp source to make the wavelength band of the electromagnetic wave radiated therefrom to an appropriate

wavelength band (that is, a wavelength band having a high absorption coefficient of the semiconductor film). Accordingly, the substrate 101 itself is not distorted and deformed. For example, a halogen lamp having a spectrum peak in a band of wavelengths longer than 600 nm is suitable for heating the amorphous silicon film. By
5 crystallizing the semiconductor film having the amorphous structure in this way, the crystalline silicon film 104 can be obtained as well.

[0024]

As described above, the crystalline silicon film 104 can be formed on the glass substrate 101. Next, an amorphous silicon film 105 containing a rare gas element is
10 formed on the crystalline silicon film 104, as illustrated in FIG. 1(B). As a typical example, an amorphous silicon film containing 1×10^{19} to 1×10^{22} /cm³ of argon as the rare gas element is formed by a sputtering method, so as to have a thickness of 0.05 to 0.1 μ m. In the sputtering, highly pure silicon is used as a target and argon or argon and hydrogen is used as a sputtering gas to form the amorphous silicon film. In order
15 to incorporate a large amount of argon into the film, it is essential to control the pressure at the time of forming the film. Detailed conditions depend on the used machine. For example, by setting the pressure at the time of forming the film to 0.2 to 1 Pa and making film-forming speed relatively slow, the argon content can be made large.

[0025]

20 Of course, the rare gas element which can be used is not limited to argon. There may be used helium, krypton, neon or xenon. The production method of the amorphous silicon film 105 is not limited to a sputtering method. A plasma CVD method or a vapor deposition method may be used if it causes the rare gas element to be incorporated at the same concentration.

[0026]

Thereafter, an electrically heating furnace is used to conduct heat treatment at 450 to 800 °C, preferably at 550 °C, in a nitrogen atmosphere for 1 to 4 hours so that the amorphous silicon film 105 containing the rare gas element becomes a gettering site.

5 Thus, the concentration of the catalyst element (here, nickel) contained in the crystalline silicon film 104 can be made to $2 \times 10^{18} \text{ cm}^3$ or less. At this time, the catalyst element moves in the direction shown by an arrow in FIG. 1(B), so as to be concentrated and collected in the amorphous silicon film 105 containing the rare gas element.

[0027]

10 In the case that an RTA method is used, a heating lamp source is lighted for 1 to 60 seconds, preferably 30 to 60 seconds. This is repeated 1 to 10 times, preferably 2 to 6 times. The emission intensity of the lamp source may be freely decided; however, the intensity is set in such a manner that the semiconductor film is instantaneously heated up to about 600 to 1000 °C, preferably about 700 to 750 °C.

15 [0028]

Thereafter, the amorphous semiconductor film 107 is etched to be removed. This etching is performed by dry etching using NF_3 or CF_4 , dry etching using ClF_3 without using plasma, or wet etching using an alkali solution such as an aqueous solution containing hydrazine or tetraethylammonium hydroxide (chemical formula:
20 $(\text{CH}_3)_4\text{NOH}$).

[0029]

By this etching treatment, the surface of the crystalline silicon film 104 is exposed. An n-type crystalline silicon film 106 is formed on this surface. The n-type crystalline silicon film 106 may be formed by a plasma CVD method or a

reduced-pressure thermal CVD method. It is advisable to form the n-type crystalline silicon film 106 so as to have a thickness of 0.02 to 0.2 μm , typically a thickness of 0.1 μm . Next, a transparent electrode 107 is formed on the n-type crystalline silicon film 106. As the transparent electrode 107, indium tin oxide alloy (ITO) with a thickness of
5 0.08 μm is formed by a sputtering method (FIG. 1(C)).

[0030]

Next, a step of providing lead-out electrodes 108 and 109 is conducted. At the time of providing the lead-out electrodes 108 and 109, parts of the transparent electrode 107, the n-type crystalline silicon 105 and the crystalline silicon 103 are
10 removed, as illustrated in FIG. 1(E). Metal films made of aluminum, silver or the like are formed by a sputtering method or a vacuum evaporation method, to provide a positive electrode 108 on the crystalline silicon film 104 and provide a negative electrode 109 on the transparent electrode 107. The lead-out electrodes 108 and 109 can be formed, using aluminum, silver, silver paste or the like.

15 [0031]

After the lead-out electrodes 108 and 109 are provided, heat treatment is conducted at 150 to 300 $^{\circ}\text{C}$ for several minutes to improve adhesion between the crystalline silicon film 104 and the silicon oxide film 102 as the base film. Thus, good electric properties can be gained. Specifically, an oven is preferably used to conduct
20 heat treatment at 200 $^{\circ}\text{C}$ in a nitrogen atmosphere for 30 minutes. By the above-mentioned process, a photoelectric conversion device can be obtained.

[0032]

[Embodiment 2]

According to the method for producing a photoelectric conversion device of the

present embodiment, in the step of removing the catalyst element for promoting the crystallization of silicon after crystallization, a method of using ion implantation or ion doping is adopted to add a rare gas element into the surface of the crystalline silicon film.

5 [0033]

In FIG. 2, a silicon oxide film 202 is formed as a base film on a glass substrate 201 to have a thickness of 0.3 μm . This silicon oxide film is formed by a plasma CVD method using tetramethyl silicate (TEOS) as raw material. It can be formed by a sputtering method as another method. Next, silane gas is used as raw material to form
10 an amorphous silicon film 203 by a plasma CVD method. Next, the substrate is immersed into ammonium hydrogen peroxide, and kept at 70 °C for 5 minutes, thereby forming an oxide film (not illustrated) on the surface of the amorphous silicon film 203. A solution of acetate nickel is applied onto the surface of the amorphous silicon film 203 by a spin coating method. The nickel element functions as an element for
15 promoting crystallization in crystallizing the amorphous silicon film 203.

[0034]

Next, it is kept at 450 °C in a nitrogen atmosphere for 1 hour to release hydrogen in the amorphous silicon film 203. In the nitrogen atmosphere, it is subjected to heat treatment at 550 °C for 4 to 8 hours, to crystallize the amorphous
20 silicon film 203. In this way, a crystalline silicon film 204 is obtained. The steps described above are performed in the same way as in the embodiment 1.

[0035]

Thereafter, ion doping is used to add a rare gas element to the crystalline silicon film 204. As the rare gas element, argon is used. The dosage thereof is set to

1×10^{14} to 1×10^{17} /cm², typically 2×10^{15} /cm², and acceleration voltage is set to 10 keV. By this doping treatment, a region containing argon at a concentration of 1×10^{18} /cm³ or more is formed in a region 205 having a depth of about 0.1 μm from the surface of the crystalline silicon film 204 (FIG. 2(B)).

5 [0036]

Thereafter, heat treatment is conducted to subject nickel remaining in the crystalline silicon film 204 to gettering. In the case of using an electrically heating furnace, it is conducted at 500 to 800 °C, preferably 550 °C, in a nitrogen atmosphere for 1 to 4 hours. It can be also performed by an RTA method. The region 205 into
10 which the rare gas is implanted has an amorphous structure wherein the crystal is broken. A strain field is generated in this region 205 by implanting argon thereinto, which has a larger atomic diameter than that of silicon. Thus, it can be made to a gettering site. Following the heat treatment, nickel in the crystalline silicon film 204 moves into this region 205 so that the concentration of the nickel element in the
15 crystalline silicon film 204 can be made to 2×10^{18} /cm³ or less.

[0037]

A 100-ppm nickel acetate solution was applied to an amorphous silicon film having a thickness of 300 nm, and then the film was crystallized by heat treatment (i.e., annealing) at 550 °C for 4 hours to obtain a crystalline silicon film. A rare gas, argon,
20 was implanted to the crystalline silicon film by an ion doping method at an acceleration voltage of 10 keV and a dosage of 2×10^{15} /cm². The distribution of argon at this time was measured by secondary ion mass spectrometry. Argon was implanted from the surface of the crystalline silicon film to a depth of about 80 nm. The concentration thereof was 1×10^{18} /cm³ or more. FIG. 6 also shows a profile after the

same sample was subjected to heat treatment at 550 °C for 4 hours. The concentration distribution of argon hardly changed. The argon content in the film did not change. It is therefore understood that argon was not released again outside the film at this temperature. The fact that argon is not distributed again by heat treatment
5 demonstrates that the gettering site can be stably kept, that is, that if the argon-added region is removed, no bad effect is produced on the crystalline silicon film, as will be described later.

[0038]

FIG. 7 shows data obtained by measuring a nickel concentration distribution in
10 the same sample by secondary ion mass spectrometry. By heat treatment at 550 °C for 4 hours, the concentration of nickel in the film was reduced from $5 \times 10^{18} / \text{cm}^3$ to $1 \times 10^{18} / \text{cm}^3$. The reduced nickel moved to the region to which argon was added (the region having a depth of about 80 nm from the surface of the crystalline silicon film). The concentration in this region increased from $1.2 \times 10^{19} / \text{cm}^3$ to $6 \times 10^{19} / \text{cm}^3$ as
15 the peak value thereof. As described above, the data shown in FIG. 7 clearly demonstrate the effect of the gettering by argon. Of course, such a gettering effect can be produced by not only argon but also any other rare gas elements.

[0039]

Furthermore, the region 205 to which argon is added at the high concentration
20 is not recrystallized by this heat treatment. Consequently, the strain field remains as it is and it becomes a good gettering site for gettering.

[0040]

Accordingly, in order to complete a photoelectric conversion device, it is necessary to remove the region 205. The etching may be performed in the same way

as in the embodiment 1. After removing about 0.1 μm from the surface of the crystalline silicon film 204, an n-type crystalline silicon film 206 is formed. The n-type crystalline silicon film 206 may be formed by a plasma CVD method or a reduced-pressure thermal CVD method. The thickness of the n-type crystalline silicon
5 film 206 is preferably set to 0.02 to 0.2 μm , and is typically set to 0.1 μm . Furthermore, a transparent electrode 107 is formed. As the transparent electrode 106, an indium tin oxide alloy (ITO) with a thickness of 0.08 μm is formed by a sputtering method (FIG. 2(C))

[0041].

10 In order to form lead-out electrodes 208 and 209, parts of the transparent electrode 207, the n-type crystalline silicon 206 and the crystalline silicon 204 are removed, as illustrated in FIG. 2(D) to partially expose the surface of the crystalline silicon film 204. Metal films made of aluminum, silver or the like are formed by a sputtering method or a vacuum evaporation method, to provide a positive electrode 208
15 on the crystalline silicon film 204 and provide a negative electrode 209 on the transparent electrode 207.

[0042]

After the lead-out electrodes 208 and 209 are provided, heat treatment is conducted at 150 to 300 $^{\circ}\text{C}$ for several minutes to improve adhesion between the
20 crystalline silicon film 204 and the silicon oxide film 202 as the base film. Thus, good electric properties can be gained. In the present embodiment, an oven is used to conduct heat treatment at 200 $^{\circ}\text{C}$ in a nitrogen atmosphere for 30 minutes. By the above-mentioned process, a photoelectric conversion device can be completed.

[0043]

[Embodiment 3]

The following will describe an example of an embodiment wherein an amorphous silicon film formed as a gettering site on a crystalline silicon film formed
5 using a catalyst element is selectively removed.

[0044]

Referring to FIG. 5(A), a silicon oxide film 502 is formed as a base film on a substrate 501 in the same way as in the embodiment 1, so as to have a thickness of 0.3 μm . Next, an amorphous silicon film is made from silane gas as raw material by a
10 plasma CVD method, and then a catalyst element is introduced thereto so as to crystallize it. In this way, a crystalline silicon film 503 is formed. The steps described above are performed in the same way as in the embodiment 1.

[0045]

Next, a barrier layer 504 is formed on the surface of the crystalline silicon film
15 503. To form the barrier layer, a chemical oxide produced by treatment with ozone water may be used. The chemical oxide may also be produced by treatment with an aqueous solution wherein hydrogen peroxide water is mixed with sulfuric acid, hydrochloric acid, nitric acid or the like. In a different method, the chemical oxide may be produced by plasma treatment in an oxidizing atmosphere or oxidizing
20 treatment with ozone generated by irradiation of ultraviolet rays in an oxygen-containing atmosphere. Alternatively, it may be heated at 200 to 350 °C in a clean oven to form a thin oxidized film as the barrier layer, or an oxidized film having a thickness of about 1 to 5 nm is deposited as the barrier layer by a plasma CVD method, a sputtering method or a vapor deposition method.

[0046]

Thereafter, an amorphous silicon film 505 containing a rare gas element is formed on the barrier layer 504. This film may be formed in the same way as in the embodiment 1. Alternatively, after the formation of an amorphous silicon film, the rare gas element may be added thereto by an ion implantation method or an ion doping method, as described in Embodiment 2. This amorphous silicon film 505 is used as a gettering site.

[0047]

In order to subject the catalyst element remaining in the crystalline silicon film 503 to gettering, heat treatment is conducted. The heat treatment is conducted at 500 to 800 °C, preferably 550 °C, in a nitrogen atmosphere for 1 to 4 hours. In the case that an RTA method is used, a heating lamp source is lighted for 1 to 60 seconds, preferably 30 to 60 seconds. This is repeated 1 to 10 times, preferably 2 to 6 times. The emission intensity of the lamp source may be freely decided; however, it is set in such a manner that the semiconductor film is instantaneously heated up to about 600 to 1000 °C, preferably about 700 to 750 °C.

[0048]

Thereafter, the amorphous silicon film 505 is selectively etched to be removed. This etching can be performed by dry etching using ClF_3 without the use of plasma, or wet etching using an alkali solution such as an aqueous solution containing hydrazine or tetraethylammonium hydroxide (chemical formula: $(\text{CH}_3)_4\text{NOH}$). At this time, the barrier layer 504 functions as an etching stopper. Thereafter, the barrier layer 504 may be removed with hydrofluoric acid.

[0049]

In this way, the catalyst element in the crystalline silicon film 503 is gettered into the amorphous silicon film 505 to which the rare gas element is added, so as to make it possible to set the concentration of the catalyst element in the crystalline silicon
5 film 503 to $2 \times 10^{18} / \text{cm}^3$ or less.

[0050]

An n-type crystalline silicon film 506 is formed on the surface thereof. The n-type crystalline silicon film 506 may be formed by a plasma CVD method or a reduced-pressure thermal CVD method. The thickness of the n-type crystalline silicon
10 film 506 is set to 0.02 to 0.2 μm . Next, as a transparent electrode 507, an indium tin oxide alloy (ITO) having a thickness of 0.08 μm is formed on the n-type crystalline silicon film 506 by a sputtering method (FIG. 5(B)).

[0051]

Furthermore, a step of providing lead-out electrodes 508 and 509 is conducted.
15 At the time of providing the lead-out electrodes 508 and 509, parts of the transparent electrode 507, the n-type crystalline silicon 506 and the crystalline silicon film 503 are removed, as illustrated in FIG. 5(C). Metal films made of aluminum, silver or the like are formed by a sputtering method or a vacuum evaporation method, to provide a positive electrode 508 on the crystalline silicon film 503 and provide a negative
20 electrode 509 on the transparent electrode 506. The lead-out electrodes 508 and 509 can be formed, using aluminum, silver, silver paste or the like.

[0052]

After the lead-out electrodes 508 and 509 are provided, heat treatment is conducted at 150 to 300 $^{\circ}\text{C}$ for several minutes to improve adhesion between the

crystalline silicon film 503 and the silicon oxide film 502 as the base film. Thus, good electric properties can be gained. In the present embodiment, an oven is used to conduct heat treatment at 200 °C in a nitrogen atmosphere for 30 minutes. By the above-mentioned process, a photoelectric conversion device can be completed. The present embodiment can be combined with the embodiment 1 or embodiment 2.

[0053]

[Embodiment 4]

The present embodiment shows an example of an embodiment wherein the surface of the crystalline silicon film is subjected to anisotropic etching in the process for producing the photoelectric conversion device described as the embodiments 1 to 3, so as to make I layer in the photoelectric conversion device uneven as shown in FIG. 3. The technique wherein the surface is made uneven to reduce the surface reflection of the photoelectric conversion device is called texture treatment.

[0054]

A silicon oxide film is formed as a base film 302 on a glass substrate 301 (for example, a Corning 7959 glass substrate) to have a thickness of 0.3 μm. This silicon oxide film is formed by a plasma CVD method using tetramethyl silicate (TEOS) as raw material. It can be formed by a sputtering method as another method. Next, an amorphous silicon film is formed by a plasma CVD method. This amorphous silicon film may be formed by a reduced-pressure thermal CVD method, a sputtering method or a vacuum evaporation method as well as a plasma CVD method. The amorphous silicon film may be a substantially intrinsic amorphous silicon film, or an amorphous silicon film to which 0.001 to 0.1 atomic % of boron (B) is added. The thickness of the amorphous silicon film is set to 20 μm. Of course, this thickness may be changed

to a desired thickness by an implementor.

[0055]

Heat treatment is conducted to form a crystalline silicon film 303. In the crystalline silicon film 303, the concentration of the catalyst element introduced in the
5 step of the crystallization is reduced to $2 \times 10^{18} / \text{cm}^3$ or less by the gettering treatment of the present invention.

[0056]

After finishing the gettering treatment, the surface of the crystalline silicon film 303 is subjected to a texture treatment. The texture treatment can be conducted using
10 hydrazine or an aqueous solution of sodium hydroxide. The following will describe a case in which sodium hydroxide is used.

[0057]

The texture treatment is conducted by heating an aqueous solution having a sodium hydroxide concentration of 2% to 80 °C. Under this condition, the etching rate
15 of the crystalline silicon film 303 used in the present embodiment can be about 1 $\mu\text{m}/\text{minute}$. The etching is performed for 5 minutes. Thereafter, it is immersed into boiling water in order to stop the reaction instantaneously. Furthermore, it is sufficiently washed with flowing water. When the surface of the crystalline silicon film 303 after the texture treatment is observed with an electron microscope,
20 irregularities, which are arranged at random and have a height of about 0.1 to 5 μm , can be observed.

[0058]

An n-type crystalline silicon film 304 is formed on this surface. The n-type crystalline silicon film 304 may be formed by a plasma CVD method or a

reduced-pressure CVD method. The thickness of the n-type crystalline silicon film 304 is preferably set to 0.02 to 0.2 μm . In the present embodiment, the thickness is set to 0.1 μm .

[0059]

5 Next, a transparent electrode 305 is formed on the n-type crystalline silicon film 304. As the transparent electrode 305, an indium tin oxide alloy (ITO) having a thickness of 0.08 μm is formed by a sputtering method. Finally, a step of providing lead-out electrodes is conducted. In order to provide the lead-out electrodes, parts of the transparent electrode, n-type crystalline silicon and the crystalline silicon film 303
10 are removed and subsequently a negative electrode 306 is provided on the transparent electrode 304 and a positive electrode 306 is provided on the crystalline silicon film 303, to obtain a structure as illustrated in FIG. 3. The lead-out electrodes 306 may be formed by a sputtering method or a vacuum evaporation method using aluminum, silver, silver paste or the like. After the electrodes 306 are provided, heat treatment is
15 conducted at 150 to 300 $^{\circ}\text{C}$ for several minutes to improve adhesion between the crystalline silicon film 303 and the base film 302. Thus, good electric properties can be gained. In the present embodiment, an oven is used to conduct heat treatment at 200 $^{\circ}\text{C}$ in a nitrogen atmosphere for 30 minutes. By the above-mentioned process, a photoelectric conversion device having, in the surface thereof, a texture structure can be
20 obtained. The present embodiment can be freely combined with the embodiments 1 to 3.

[0060]

[Embodiment 5]

The present embodiment shows a technique of forming a coating film made of

a catalyst element for promoting the crystallization of silicon on a substrate, forming an amorphous silicon film closely onto the coating film made of the catalyst element, crystallizing the amorphous silicon film by heat treatment, and after the crystallization, removing the catalyst element diffused into the crystalline silicon film to produce a photoelectric conversion device, as shown in FIG. 4.

[0061]

First, a coating film made of a catalyst element for promoting the crystallization of silicon is formed on a substrate. As the catalyst element, nickel is typically used. A silicon oxide film having a thickness of 0.3 μm is firstly formed as a base film 402 on a glass substrate (for example, a Corning 7059 glass substrate) 401. This silicon oxide film is formed by a plasma CVD method using tetramethyl silicate (TEOS) as raw material. This film can be formed by a sputtering method as another method. Next, a nickel film 407 is formed on the substrate. The nickel film is formed by an electron beam vacuum evaporation method using a tablet made of pure nickel, so as to have a thickness of 0.1 μm . Next, an amorphous silicon film (amorphous silicon film) is formed by a plasma CVD method. The formation of the amorphous silicon film may be performed using a reduced-pressure thermal CVD method, a sputtering method or a vacuum evaporation method as well as a plasma CVD method. The amorphous silicon film 103 may be an amorphous silicon film to which no element of the 13 or 15 group in the periodic table is added, or an amorphous silicon film to which 0.001 to 0.1 atomic % of boron (B) is added. The thickness of the amorphous silicon film is set to 10 μm . Of course, this thickness may be changed to a desired thickness by an implementor.

[0062]

Next, it is kept at a temperature of 450 °C in a nitrogen atmosphere for 1 hour to release hydrogen in the amorphous silicon film. This is performed to lower the threshold energy for subsequent crystallization by forming dangling bonds intentionally
5 in the amorphous silicon film. Thereafter, it is subjected to heat treatment at 550 °C in the nitrogen atmosphere for 4 to 8 hours, so as to crystallize the amorphous silicon film. In this way, a crystalline silicon film 403 is obtained. Because of the catalyst action of nickel element, the temperature for this crystallization can be made to 550 °C. This crystalline silicon film 403 that has been crystallized contains 0.001 atomic % to 5
10 atomic % of hydrogen. The nickel element diffuses partially from the nickel film 407 to the silicon film, so that the crystallization advances. In this way, the crystalline silicon film 403 can be formed over the glass substrate.

[0063]

Thereafter, a gettering site is formed to perform gettering. The gettering site
15 can be formed from an amorphous silicon film containing a rare gas element, or a region to which a rare gas is implanted may be formed in the crystalline silicon film 403. Thereafter, heat treatment is conducted to perform gettering. The gettering site which has been unnecessary is removed by etching.

[0064]

20 In this way, the surface of the crystalline silicon film 403 is exposed over the main surface of the substrate 401. An n-type crystalline silicon film 404 is formed on this surface. Next, as a transparent electrode 405, an indium tin oxide alloy (ITO) having a thickness of 0.08 μm is formed on the n-type crystalline silicon film 404 by a sputtering method. Finally, a step of providing lead-out electrodes 406 is conducted to

complete a photoelectric conversion device. The structure of the present embodiment may be freely combined with the embodiments 1 to 4.

[0065]

[Effect of the Invention]

5 By the method for producing a photoelectric conversion device according to the present invention, a crystalline silicon film can be obtained at a lower heat treatment temperature than ever before by using a catalyst material such as nickel in the step of
10 subjecting an amorphous silicon film to heat treatment so as to be crystallized. Additionally, the concentration of the catalyst material remaining in the resultant crystalline silicon film can be reduced. As a result, it is possible to obtain a photoelectric conversion device using an inexpensive glass substrate and exhibiting a superior photoelectric conversion characteristic.

[Brief Description of the Drawings]

[FIG. 1] A view which schematically illustrates a method for producing a photoelectric
15 conversion device of the present invention.

[FIG. 2] A view which schematically illustrates a method for producing a photoelectric conversion device of the present invention.

[FIG. 3] A view which illustrates an example of a cross sectional structure of the photoelectric conversion device of the present invention.

20 [FIG. 4] A view which illustrates an example of a cross sectional structure of the photoelectric conversion device of the present invention.

[FIG. 5] A view which schematically illustrates a method for producing a photoelectric conversion device of the present invention.

[FIG. 6] A graph showing a concentration distribution of argon added to a crystalline

silicon film by an ion doping method.

[FIG. 7] Data showing concentration distributions of nickel added to a crystalline silicon film and a graph showing changes before and after heat treatment.

[Document Name] Abstract

[Abstract]

[Problem] Since a catalyst material used for crystallization is a material unpreferable for a crystalline silicon film, it is required to be made at a concentration as possible after crystallization. In the case that silicon has many defect levels, carriers generating light are trapped into the defect levels to become extinct, thereby deteriorating the photoelectric conversion characteristic. An object of the present invention is to crystallize silicon using a catalyst element and to improve characteristics of a photoelectric conversion device by crystallizing silicon with a catalyst element and removing the catalyst element that has been unnecessary after crystallization.

[Solving Means] A catalyst element remaining in a first semiconductor film after crystallization can be moved into a second semiconductor film and concentrated and collected by forming the second semiconductor film containing a rare gas element thereon and then conducting a second heat treatment. That is, by incorporating the rare gas element into the second semiconductor film, a strain field can be generated so as to be a gettering site. Since the rare gas element is not basically bonded to another atom, it is inserted between lattices in the semiconductor film, thereby generating the strain field.

[Selected drawings] FIG. 1